Second-harmonic generation circular-dichroism spectroscopy from chiral monolayers

J. D. Byers, H. I. Yee, T. Petralli-Mallow, and J. M. Hicks

Department of Chemistry, Georgetown University, Washington, DC 20057

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The second-harmonic-generation (SHG) efficiency from a monolayer of oriented chiral molecules (R- or S-2,2'-dihydroxyl-1,1'binaphthyl) has a strong dependence upon the handedness of the circularly polarized excitation beam. The SHG circular-dichroism (CD) effect is much larger than in ordinary CD spectroscopy because SHG-CD is electric dipole allowed. The technique allows the study of chiral surfaces. The preference for left or right circularly polarized light is dependent on both the chirality (R or S) and the absolute orientation of the molecules (pointed up or down).

Chemists have long been interested in the symmetries of molecules; however, chiral surfaces have not yet been the subject of much investigation. Chiral surfaces are of interest in fields such as synthesis of asymmetric chemical species, separation of chiral compounds, crystal growth, and the adsorption of proteins at interfaces. The most common method for the study of chirality is spectroscopy based on optical activity, for example, circular-dichroism (CD) spectroscopy and optical rotatory dispersion (ORD).[1] The theory of these spectroscopies centers on the rotational strength R, which results from a very weak interaction between the electric and magnetic dipole transition moments within a molecule.[2] As with most linear (single-photon) spectroscopic methods, CD and ORD are not particularly surface sensitive.

Recently, we reported the appearance of a circular dichroic effect in surface second-harmonic generation (SHG).[3] Second-order nonlinear optical methods such as SHG have been shown to be sensitive to interfaces.[4] In centrosymmetric media, SHG is electric dipole forbidden; however, it is electric dipole allowed at a surface where symmetry is broken. The second-order polarization of a surface layer induced by an intense light field can be expressed as $\mathbf{P}^{(2)} = \chi^{(2)} : \mathbf{E}_\omega \mathbf{E}_\omega$, where $\chi^{(2)}$ is the second-order susceptibility of the surface layer. For incident radiation of frequency ω, the resulting nonlinear polarization of the surface layer has been shown to emit a second-harmonic wave of frequency 2ω in the reflected direction.[5] Surface SHG has been used to investigate submonolayer concentrations of adsorbates at a variety of interfaces.[6] Detailed structural, kinetic, and spectroscopic information has been obtained.[7]

For circularly polarized light incident at a monolayer consisting of the chiral R-2,2'-dihydroxy-1,1'binaphthyl (BN), the SHG efficiency was shown to depend strongly on the handedness of the light. In contrast to ordinary CD effects, where the difference in absorbance for left versus right circularly polarized light is on the order of 0.1% of the average absorbance (i.e., $(A_l - A_r)/A = 0.001$), the SHG-CD varied by up to 100% on resonance

$$\left[I_{\text{SHG-CD}} = \frac{(I_{\text{left}}^{\text{SHG}} - I_{\text{right}}^{\text{SHG}})}{[\frac{1}{2}(I_{\text{right}}^{\text{SHG}} + I_{\text{left}}^{\text{SHG}})]} = 1.0 \right] .$$

In this paper, we report several key experiments along with the theory demonstrating that SHG-CD from a chiral surface arises from electric dipole-allowed $\chi^{(2)}$ terms related directly to molecular properties of the medium. The electric dipole origin of SHG-CD is in contrast to ordinary CD spectroscopy, which relies on the very small rotational strength R. The rotational strength can be written as $R = \text{Im}\{\mu \cdot \mathbf{m}\}$, where μ and $\mathbf{m}$ are the electric dipole transition moment and the magnetic dipole transition moment, respectively.[2] SHG-CD is a large effect that depends on the handedness of the chromophore, thereby revealing chirality, and in addition, it possesses submonolayer surface sensitivity.[3]

In a typical surface SHG geometry, the intensity of the reflected second-harmonic wave is

$$I_{2\omega} = \frac{32\pi^3 \omega^2}{c^3} \sec^2\theta |\varepsilon_{2\omega} \cdot \chi^{(2)} : \varepsilon_\omega \varepsilon_\omega|^2 I_\omega^2 , \tag{1}$$

where θ is the angle of the incident wave measured from the surface normal.[8,9] ε_ω and $\varepsilon_{2\omega}$ are the Fresnel-corrected polarization vectors of the ω and 2ω electric fields in the surface layer. $\chi^{(2)}$ is a tensor defined by

$$P_i^{(2)} = \sum_{jk} \chi_{i,j,k}^{(2)} E(\omega)_j E(\omega)_k . \tag{2}$$

For an isotropic surface invariant with rotations about the perpendicular z axis, the 27 elements of the third-rank tensor $\chi^{(2)}$ can be reduced to four nonzero and independent elements:[10,11]

$$\chi^{(2)} = \begin{bmatrix} 0 & 0 & \chi_3 & 0 & 0 & -\chi_4 & \chi_2 & 0 & 0 \\ 0 & 0 & \chi_4 & 0 & 0 & \chi_3 & 0 & \chi_2 & 0 \\ \chi_3 & \chi_4 & 0 & -\chi_4 & \chi_3 & 0 & 0 & 0 & \chi_1 \end{bmatrix} , \tag{3}$$

where

$$\chi_1 = \chi_{zzz} ,$$

$$\chi_2 = \chi_{zxx} = \chi_{zyy} , \tag{4}$$

$$\chi_3 = \chi_{xzx} = \chi_{xxz} = \chi_{yzy} = \chi_{yyz} ,$$

$$\chi_4 = \chi_{xzy} = \chi_{xyz} = -\chi_{yzx} = -\chi_{yxz} .$$

The coordinate axes x, y, and z are defined in Fig. 1. For isotropic surfaces of achiral molecules, there are an infinite number of mirror planes of symmetry, thus the fourth term vanishes. For surfaces of chiral molecules, mirror planes of symmetry do not exist and all elements of Eq. (4) are necessary to describe the nonlinear behavior of the surface layer.

Using Eq. (1) and assuming negligible Fresnel corrections,[12] the s and p components of the reflected second-harmonic wave from chiral surfaces are

$$I_{2\omega}^s = \frac{32\pi^3\omega^2}{c^3}\tan^2\theta|\chi_3 s_\omega p_\omega - \chi_4 p_\omega p_\omega \cos\theta|^2 I_\omega^2 \ , \tag{5a}$$

$$I_{2\omega}^p = \frac{32\pi^3\omega^2}{c^3}\tan^2\theta|\chi_1 p_\omega p_\omega \sin^2\theta + \chi_2 s_\omega s_\omega + \chi_1 p_\omega p_\omega \cos^2\theta + 2\cos\theta(\chi_4 s_\omega p_\omega - \chi_3 p_\omega p_\omega \cos\theta)|^2 I_\omega^2 \ , \tag{5b}$$

where s_ω and p_ω are the s and p components of the incident polarization vector ε_ω. The polarization of the incident wave can be defined in terms of a polarization angle γ and a phase difference δ:

$$\varepsilon_\omega = s_\omega \cdot \hat{s} + p_\omega \cdot \hat{p} = \sin\gamma\hat{s} + e^{i\delta}\cos\gamma\hat{p} \ . \tag{6}$$

For circularly polarized incident light $\gamma = 45°$ and $\delta = \pm 90°$, with the positive sign representing right circular polarization and the negative sign representing left circular polarization. The intensities for s and p components of the reflected second-harmonic wave from circularly polarized incident light become

$$I_{2\omega}^s = \frac{32\pi^3\omega^2}{c^3}\tan^2\theta|\pm i\chi_3 - \chi_4\cos\theta|^2 I_\omega^2 \ , \tag{7a}$$

$$I_{2\omega}^p = \frac{32\pi^3\omega^2}{c^3}\tan^2\theta|\tfrac{1}{2}(\chi_2 - \chi_1)\sin^2\theta$$

$$+ \cos\theta(\chi_3\cos\theta \pm i\chi_4)|^2 I_\omega^2 \ , \tag{7b}$$

where the upper sign represents right circularly polarized incident light, and the lower sign represents left. Note that for linearly polarized input radiation, [$\gamma = 45°, \delta = 0°$ in Eq. (6)], Eqs. (5a) and (5b) reduce to those previously derived.[11]

From these expressions, it can be seen that the polarization-analyzed SHG output will depend on the relative magnitudes and signs of the four $\chi^{(2)}$ tensor elements. For example, a dichroic effect in the s-polarized output of the SHG signal at a given wavelength will result if χ_3 and χ_4 are of similar magnitude and either element has a significant imaginary component. If $\chi_3 \gg \chi_4$

or vice versa, then the dichroic effect would be too small to be observed. Also, if both χ_3 and χ_4 are purely real then there are no cross terms in the squaring in Eq. (7), and the dichroic effect is absent. Prior to our work, to our knowledge the ramifications of having a chiral surface in which χ_3 and χ_4 are comparable had not been explored.

The macroscopic tensor elements $\chi_{ijk}^{(2)}$ relate to the microscopic description of the interfaces, and thus to information such as the chirality and orientation of individual molecules. In the electric dipole approximation the macroscopic susceptibility tensor $\chi^{(2)}$ can be written as the sum of the microscopic nonlinear polarizabilities $\alpha^{(2)}$ of the surface molecules:[11,13]

$$\chi_s^{(2)} = N_s\langle\alpha^{(2)}\rangle \ . \tag{8}$$

Here N_s is the surface density of the SHG active molecules, and local-field effects have been omitted.[14-16] The brackets represent geometric averaging over all molecular orientations.

The chirality of the surface molecules can be probed by measuring the SHG-CD from the surface layer. Two monolayers that differ only in chirality (one is made of the R enantiomer, and the other of the S) will have opposite preferences for the handedness of the excitation light (i.e., the sign of $I_{\text{SHG-CD}}$ will be opposite). This results because the two enantiomers have χ_4 elements of opposite sign[17] and achiral elements (χ_1, χ_2, and χ_3) of the same sign. If one enantiomer preferred left over right circularly polarized light for generating second-harmonic signals ($I_{\text{SHG-CD}} > 0$) then, from Eq. (7a), χ_3 and χ_4 must have the same sign for that enantiomer. For the other enantiomer χ_3 and χ_4 will have opposite signs. From Eq. (7a) it can be seen that the preference will then be for right over left circularly polarized light ($I_{\text{SHG-CD}} < 0$).

In order to experimentally verify the dichroic effect in the s-polarized SHG signal,[18] SHG efficiencies for left and right circularly polarized light were measured in reflection from R-BN and S-BN adsorbed at monolayer coverages on optically flat ($\lambda/10$) fused silica windows. The picosecond dye laser apparatus and sample preparation have been described.[3,19] A quartz rochon analyzer was inserted into the collection optics. The s component of the SHG signal was collected at 294 nm, close enough to resonance to ensure sizable imaginary components of
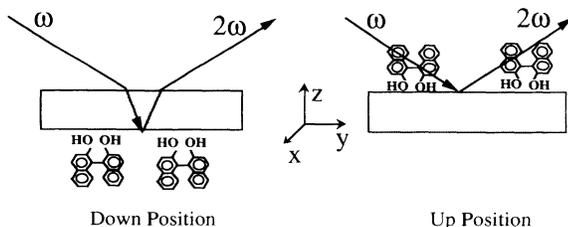

FIG. 1. Sample geometries, relative to the incident and reflected light, used to show the dependence of SHG-CD on orientation of surface molecules. Note that in both cases the same enantiomer of BN is present.

$\chi^{(2)}$. As shown in Table I, the R enantiomer prefers left circularly polarized light ($I_{\text{SHG-CD}} > 0$). Inversely, the S enantiomer prefers right circularly polarized light ($I_{\text{SHD-CD}} < 0$). We presume that the BN molecules are oriented with the hydroxyl groups toward the quartz surfaces (bound by hydrogen bonds to the surface silanols) and the orientation is the same for both the R and S enantiomers. A 50-50 mixture of R and S shows no preference for the helicity of light ($I_{\text{SHD-CD}} = 0$).

Another aspect of this theory that can be tested experimentally concerns the average orientation of the surface molecules. In previous studies of achiral molecules, the ratio $\chi_{zzz}^{(2)}/\chi_{xzx}^{(2)} = \langle \cos^3 \Theta \rangle / \langle \sin^2 \Theta \cos \Theta \rangle$ is determined, and the average tilt angle from the surface normal θ is inferred for rodlike molecules where $\alpha_{\zeta\zeta\zeta}^{(2)}$ dominates the $\alpha^{(2)}$ tensor.[16] The signs of both χ_{zzz} and χ_{xzx} change upon inversion of the molecules at the surface, so the ratio will not yield the absolute orientation (molecules pointed up or down). Determination of the sign of χ_{xzx} and hence the absolute orientation of the surface molecules requires a measurement of the phase of the SH wave relative to the incident wave.[20]

For chiral absorbates, the orientation method yielding a tilt angle cannot be used since in general one single element does not dominate $\alpha^{(2)}$. However, using the same arguments applied to the determination of the surface chirality, any change in sign of the three achiral elements without changing χ_{xyz} leads to a reversal of the SHG efficiency preference using right or left circularly polarized light. Although χ_{zzz}, χ_{zxx}, and χ_{xzx} change sign when the molecules are rotated 180° about any axis in the plane, χ_{xyz} does not change sign.[21] Therefore the sign of $I_{\text{SHG-CD}}$ will be different for molecules pointed up compared to those pointed down.

To verify this, we measured the SHG intensities of R-BN monolayers at the air-quartz interface using the two geometries shown in Fig. 1. The fundamental light was incident on the molecules from either the air side or the quartz side of the interface. Table II shows the difference signal $I_{\text{SHG-CD}}$ for the R enantiomer in both the up and down geometries. The R enantiomer prefers left circularly polarized light when in the up position, but prefers right circularly polarized light in the down position. The $I_{\text{SHG-CD}}$ sign change is the result of sign changes of the χ_{zzz}, χ_{zxx}, and χ_{xzx} elements upon 180° rotation of the sample.[22] The magnitude of the difference between the up versus down geometries is due to different incident angles and Fresnel factors for the two geometries.

The results in Tables I and II show the possibility of determining the chirality or orientation of chiral mole-

TABLE I. The circular dichroism $I_{\text{SHG-CD}}$ $= (I_{\text{left}}^{\text{SHG}} - I_{\text{right}}^{\text{SHG}})/[\frac{1}{2}(I_{\text{right}}^{\text{SHG}} + I_{\text{left}}^{\text{SHG}})]$ of the SH response as a function of molecular chirality for monolayers of BN molecules. $\lambda_{2\omega} = 294$ nm.

Surface species	$I_{\text{SHG-CD}}$
R-BN	+0.7
S-BN	−0.7
Racemic mixture	0.0

TABLE II. The circular dichroism $I_{\text{SHG-CD}}$ $= (I_{\text{left}}^{\text{SHG}} - I_{\text{right}}^{\text{SHG}})/[\frac{1}{2}(I_{\text{right}}^{\text{SHG}} + I_{\text{left}}^{\text{SHG}})]$ of the SH response as a function of sample orientation for monolayers of R-BN. $\lambda_{2\omega} = 294$ nm.

Geometry[a]	$I_{\text{SHG-CD}}$
up	+0.7
down	−1.0

[a]See Fig. 1.

cules at a surface. In our SHG-CD experiment the SH intensity is largest when the χ_{xyz} generated component is in phase with the component from the achiral elements. The phase difference is determined by the chirality of the surface molecules, their orientation (up or down), and the phase difference between the s and p components of the excitation light (left or right circular). Determination of either the chirality or orientation requires knowledge of the other. Further work is in progress to determine both the orientation and the chirality of the molecular monolayer when both are a priori unknown.

Since the dichroism of the SH response requires significant imaginary components of the $\chi^{(2)}$ elements, the effect should be observable only near resonance. The spectral properties provide important information about the nature of the species and the electronic states producing the SHG. The s component of the SHG signal from monolayers of R-BN at the air/fused-quartz interface in the up geometry was collected as a function of wavelength and incident polarization. The data for left and right circularly polarized excitation are shown in Fig. 2. There is a strong preference for left circularly polarized light, the magnitude of which varies with wavelength.

The spectral information given in Fig. 2 can be interpreted in terms of the molecular hyperpolarizability tensor $\alpha^{(2)}$ for individual BN molecules. The absorption spectrum of BN in cyclohexane is shown as the solid line in Fig. 3; there are two pairs of electronic bands in this region at about 278 and 318 nm. The fine structure is solvent dependent. Figure 3 also shows the SHG spectral dependence of $\Delta I_{\text{SHG}} = I_{\text{left}}^{\text{SHG}} - I_{\text{right}}^{\text{SHG}}$. The SHG di-
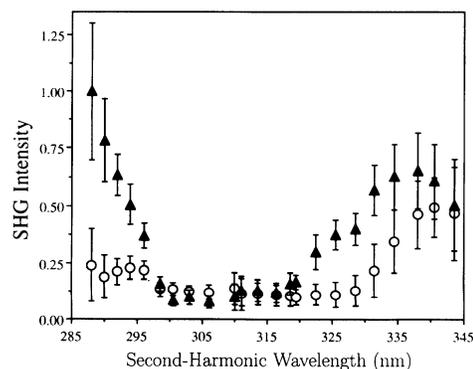

FIG. 2. Spectral dependence of s-polarized SHG from monolayers of R-BN molecules at air/fused quartz interface in the up geometry of Fig. 1 for left (▲) and right (○) circularly polarized incident light.

chroism is spectrally related to resonances in BN molecules.

In our previous work it was not known whether the SHG dichroism was of $\text{Im}\{\mu\cdot\mathbf{m}\}$ origin as in ordinary CD, or of electric dipole-allowed origin.[3] The macroscopic analysis above [Eq. (7)] and an understanding of the molecular hyperpolarizability $\alpha^{(2)}$ can be used to explain SHG-CD as an electric dipole-allowed process.

The molecular hyperpolarizability tensor $\alpha^{(2)}$ can be written using third-order perturbation theory and electric dipole transition moments as

$$\alpha_{abc}^{(2)} = \sum_i \sum_j \left[\frac{\langle 0|a|i\rangle\langle i|b|j\rangle\langle j|c|0\rangle}{(\hbar\omega_i - \hbar\omega - i\Gamma_i)(\hbar\omega_j - \hbar 2\omega - i\Gamma_j)} \right.$$
$$+ \frac{\langle 0|c|i\rangle\langle i|a|j\rangle\langle j|b|0\rangle}{(\hbar\omega_i - \hbar\omega - i\Gamma_i)(\hbar\omega_j + \hbar\omega - i\Gamma_j)}$$
$$+ \left. \frac{\langle 0|a|i\rangle\langle i|c|j\rangle\langle j|b|0\rangle}{(\hbar\omega_i + \hbar 2\omega - i\Gamma_i)(\hbar\omega_j + \hbar\omega - i\Gamma_j)} \right] ,$$

(9)

where the frequency of the incident wave is ω.[4,11] The frequencies ω_i are for the transitions from the ground state $\langle 0|$ to excited states $|i\rangle$ with the damping coefficients Γ_i. The numerator contains terms such as $\langle i|a|j\rangle$, which is the electric dipole transition moment between the states $\langle i|$ and $|j\rangle$ along the molecular axis a. For small values of Γ, the imaginary component of any $\alpha^{(2)}$ element will be negligible when the pump frequency ω or its harmonic 2ω is far from any resonance of the molecule. However, near resonance the imaginary components will increase and become large enough to interfere with the real parts. Consequently, an electric dipole-allowed circular dichroism of the SHG response will result. Similar to ordinary CD spectroscopy, circular dichroism of the SHG response requires significant imaginary $\chi^{(2)}$ components and, hence, is measurable only near resonance.

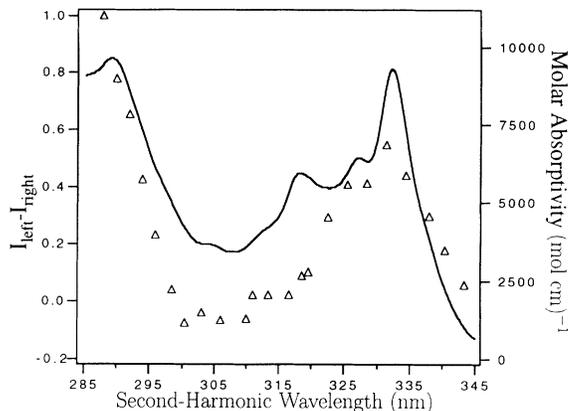Detailed analysis of the spectrum in Fig. 3 will require

FIG. 3. Solid line: absorption spectrum of 9-μM BN in cyclohexane taken on a Jasco 710 Spectropolarimeter. Triangles: spectral dependence of the circular dichroism $\Delta I_{\text{SHG}} = I_{\text{left}}^{\text{SHG}} - I_{\text{right}}^{\text{SHG}}$ of SHG from monolayers of R-BN molecules at air/fused quartz interface in the up geometry. Data are taken from Fig. 2.

knowledge of the spectral dependence of $\alpha^{(2)}$ and the distribution of molecular orientations (recall that the ordinary absorption spectrum is for an isotropic sample, whereas the surface spectrum is for an aligned sample). Further work is underway to relate the spectral SHG-CD response to molecular orbital calculations of the hyperpolarizability tensor $\alpha^{(2)}$ for BN.

In summary, it has been shown that circular dichroism spectroscopy is possible using second-order nonlinear optical effects, and that this circular dichroism is strong because it is electric dipole allowed and not dependent on the weak rotational strength ($R = \text{Im}\{\mu\cdot\mathbf{m}\}$) associated with traditional chiroptical spectroscopies. The SHG-CD method offers the advantage of being able to detect chirality at submonolayer concentrations of species. It depends upon both the orientation direction and the chirality of the surface molecules.

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$$\sigma_x \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix} \, ,$$

and Eq. (2) becomes

$$\sigma_x \vec{P}_i^{(2)} = \sum_{jk} \{ \sigma_x \vec{\chi}_{i,j,k}^{(2)} \} \{ \sigma_x E(\omega)_j \} \{ \sigma_x E(\omega)_k \} \, ,$$

noting that $\sigma_x P_x = -P_x$, $\sigma_x E_y = E_y$, and $\sigma_x E_z = E_z$. The xyz term can be written as

$$\sigma_x P_x = \sigma_x \{ \chi_{xyz} E_y E_z \}$$

and

$$-P_x = \{ \sigma_x \chi_{xyz} \} E_y E_z \, ,$$

which leads to $\sigma_x \chi_{xyz} = -\chi_{xyz}$.

[18]The signal collected in Ref. 3 consisted of all polarization components of $I_{2\omega}$.

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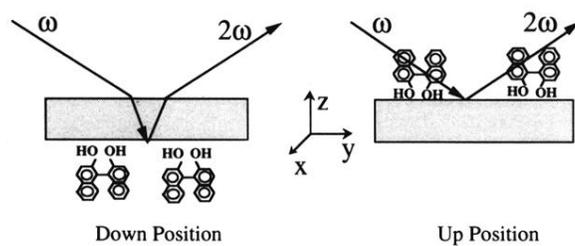
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